Supercritical Fluid Extraction–Supercritical Fluid Chromatography

Supercritical fluid extraction–supercritical fluid chromatography (SFE-SFC) is used to extract organic and some inorganic analytes from solid matrices and for the separation of organic compounds. Quantitative analysis by SFE-SFC is possible.

SFE-SFC is particularly useful for the analysis of thermally fragile compounds. SFE is often used to shorten extraction times (with respect to Soxhlet extraction) and to minimize the use of extraction solvents.

Principle of Technique

A supercritical fluid, typically CO_2, is used to extract analytes from a solid matrix. Supercritical fluids, with high diffusivities (similar to gases) and high densities (similar to liquids), are excellent fluids for the extraction of many analytes from solid matrices. The pressure and temperature of the SFE system may be controlled to change the density of the supercritical fluid and improve extraction efficiencies. Typical extraction methods use supercritical CO_2 temperatures of 40 to 150°C and pressures of 150 to 450 atm. Modifiers such as methanol and toluene are often used to improve SFE efficiencies. Modifiers may be added directly to the sample in the extraction cell, incorporated into the liquid mixture used for SFE, or continuously added to the sample cell as the supercritical fluid is flowing through the sample. The SFE effluent may be collected off-line (in an appropriate organic solvent or on a solid sorbent) for later analysis by GC, GC-MS, or LC methods, or by SFC. The SFE effluent can also be immediately introduced into the SFC if cryotrapping is used.

In SFC, extracted analytes are separated by changing temperature and pressure of the mobile phase. This affects the density, mobile-phase linear velocity, and mobile-phase composition of the fluid, usually supercritical CO_2. Columns used for SFC are typically packed with the 5- to 10-µm-i.d. particles traditionally used in HPLC analysis. SFC packing materials often contain methyl, C-8, C-18, and phenyl groups bonded to a silica backbone. SFC column dimensions range from 4.6- to 5.0-mm i.d. and from 1 to 10 m in length. After separation, the analytes are detected by a flame ionization detector.

Samples

Form. Solid samples are usually used for SFE. However, when SFE is used to extract organic compounds from water, liquid samples (or solids dissolved in liquid) are required.

Size. Sample size is limited by the capacity of the SFE cell. Typical sample sizes range from milligrams to 10 g of material.

Preparation. A solid sample is placed in an SFE cell. An appropriate modifier or drying agent is sometimes added prior to extraction. Samples must be extracted and concentrated before stand-alone SFC or GC analysis. In the integrated SFE-SFC system,

Examples of Applications

Extraction

- 2,3,7,8-TCDD from sediments and fly ash.
- Atrazine, cyanazine, and metolachlor from soil.
- Polychlorinated biphenyls and polynuclear aromatic hydrocarbons from soils and sediments.
- Actinides and lanthanides from solid materials.

SFC separation

- Enantiomers in the pharmaceutical industry.
- Components of lemon-peel oil.
- Polyunsaturated fatty acids.
- Carbon clusters C_{60} and C_{70}.
- Fossil fuel components.

SFE-SFC

- Synthetic polymers.

analytes are cryotrapped after extraction by SFE and introduced directly into the SFC system.

Limitations

SFE cell geometry and orientation can affect SFE recoveries. Efficiencies for the removal of analytes vary from one matrix to another. The SFE of analytes from spiked matrices cannot always be used to predict the conditions necessary for the extraction of native contaminants.

Modifiers must be used with CO_2 to extract polar compounds from a solid matrix. The selection of appropriate modifiers for SFE is not well understood; no systematic approach has been proposed.

NO_2 is an efficient extraction fluid. However, its use should be carefully considered because it is a strong oxidizing agent. Explosions during extraction may occur if oxidation reactions occur in the extraction cell.

The resolution of SFC is not as good as that of gas chromatography.

Estimated Analysis Time

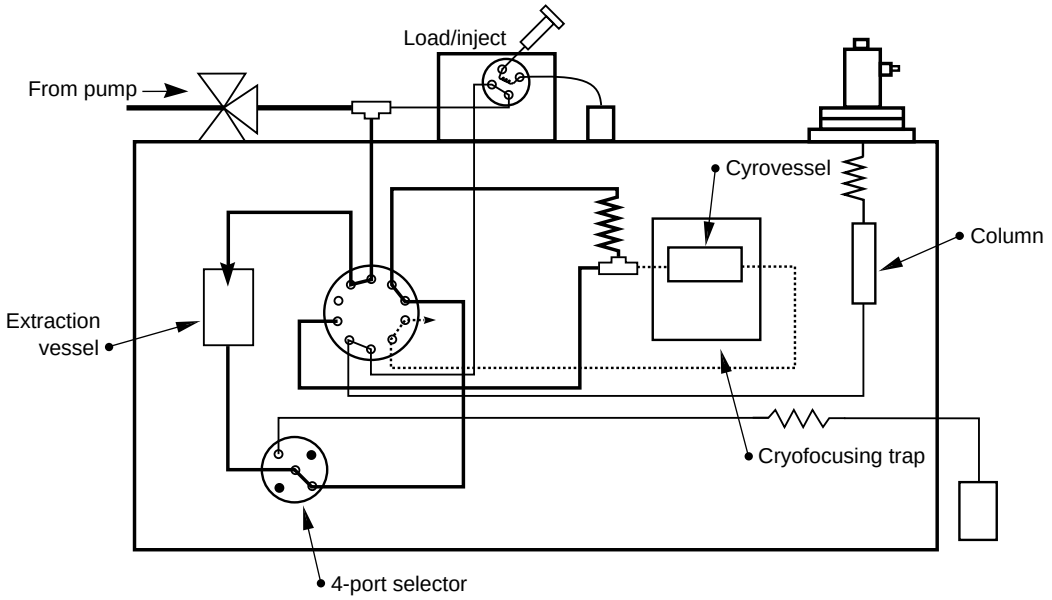
Typical SFE times range from 10 min to 2 h. SFC separations may take up to 2 h. Data analysis time depends on the complexity of the sample but generally requires less than 1 h per sample.

Capabilities of Related Techniques

Soxhlet extraction is commonly used to extract organic compounds from solid matrices.

Gas chromatography (GC) and GC-MS can be used to identify and quantitate analytes that are thermally stable, nonpolar, and volatile.

Liquid chromatography and LC-MS may be amenable to the separation of polar and thermally labile compounds; LC-MS may give more selectivity than LC alone.



The SFE-SFC system in extraction load position. This system couples sample extraction and chromatography (courtesy of Suprex).

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